Final Technical Report
on
NASA Grant NSG 1562

"Effects of High Energy Radiation on the Mechanical
Properties of Epoxy/Graphite Fiber Reinforced Composites"

by

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Report Summary

The final technical report consists of a summary listing of our

publications and the theses generated by our group that relate to composites

research. Our work on composites was initiated by a grant from NASA that

preceded NASA Grant NSG 1562 and also has been supported in part by grants

from the U.S. Army Research Office. All entries that were supported directly

by NASA Grant NSG 1562 are noted.

We have provided detailed reports of our work in previous reports. We

also include preprints of two papers that are in progress. The papers are

entitled "Effects of Ionizing Radiation on Epoxy, Graphite Fiber and

Epoxy/Graphite Fiber Composites Part I: Surface Energy Changes and Part II:

Radical Types and Radical Decay Behavior. We have approximately 60 oral

presentations made on various aspects of this work to date.

The system that has been emphasized in our work, TGDDM/DDS epoxy/Thornel

300 Graphite Fiber Composites. The mechanical properties have been shown to

be highly resistant to ionizing radiation degradation.

PUBLICATIONS, THESES DIRECTED AND PRESENTATIONS MADE BY N.C. STATE GROUP ON COMPOSITES. WORK SUPPORTED IN PART BY NATIONAL AERONAUTICS AND SPACE ADMINISTRATION AND BY THE U.S. ARMY RESEARCH OFFICE-
PRINCIPAL INVESTIGATORS: R.E. FORNES
R.D. GILBERT
J.D. MEMORY

Publications

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**Abstracts

Theses completed:

1. *Naraporn Naranong, M.S. Thesis, "Effect of High Energy Radiation on Mechanical Properties of Graphite Reinforced Composites," (1980).

2. *Kevin Schaffer, M.S. Thesis, "Characterization of a Cured Epoxy Resin Exposed to High Energy Radiation with Electron Spin Resonance," (1981).

3. *George M. Kent, M.S. Thesis, "X-ray Diffraction and ESR Studies of the Effects of high Energy Radiation on Composite Materials," (1982).

4. *Kay W. Wolf, Ph.D. Dissertation, "Effect of Ionizing Radiation on the Mechanical and Structural Properties of Graphite Fiber Reinforced Composites," (1982).

5. *Anil Netravali, Dissertation, "The Influence of Water and High Energy Radiation on the Thermal and Spectroscopical Characteristics of an Epoxy, (1984).

6. *Kab Sik Seo Dissertation, "Electron Spin Resonance Investigations and Surface Characterization of TGDDM/DDS Epoxy and T300 Graphite Fiber Exposed to Ionizing Radiation" (1985).

7. *Thomas Woodrow Wilson, III, Dissertation, "Radiation Effects on the Dynamic Mechanical Properties of Epoxy Resins and Graphite Fiber/Epoxy Composites" (1986).

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Equipment Inventory

There is no equipment in excess of $1000 purchased with funds from NASA Grant NSG 1562. However, matching contributions in the amount of $9400 from this grant has been made toward the purchase of an IBM NR100 AR FT NMR Cross polarization/Magic Angle Spinning Spectrometer. This represents about 4% of the cost of this equipment. The contribution was in lieu of student support provided by N.C. State University for work done on the grant.

Disclosure on Investigations

No inventions by our group resulted from work on this grant.

Effects of Ionizing Radiation on Epoxy,

Graphite Fiber and Epoxy/Graphite Fiber Composites

Part I: Surface Energy Changes

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Synopsis

Surface energy changes of an epoxy based on tetraglycidyl diaminodiphenyl methane (TGDDM)/diaminodiphenyl sulfone (DDS), T-300 graphite fiber and T-300/5208 (graphite fiber/epoxy) composites have been investigated after irradiation with 0.5 MeV electrons. The surface energy of TGDDM-DDS epoxy increases monotonically with radiation doses up to 1,000 Mrad mainly due to increased concentration of polar groups. IR and ESCA spectral evidence indicates that carbonyl groups are formed, probably from the tertiary hydrogen at the carbon where the -OH group is attached in the cured epoxy.

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The polarity of the graphite fiber and the graphite fiber/epoxy interface also increases with radiation dose. These results and the role of oxygen are discussed in connection with mechanical properties of epoxy/graphite fiber composites exposed to ionizing radiation.

INTRODUCTION

The mechanical integrity of composite materials is of prime importance for long-term space operations which occur in high energy radiation environments. The fiber - matrix polymer interface is an especially critical factor determining the mechanical properties of composites. The adhesion between the fiber and the matrix is controlled by many factors including (1) interlocking of polymer chains, (2) chemical bond formation, (3) polar-polar interaction, and (4) mechanical interference including frictional force or "grabbing" force generated by differential thermal shrinkage of the matrix polymer and the fiber during the curing process.[1-4]

The presence of a high concentration of free radicals in graphite fiber, presumably produced during fiber manufacture is reported in Part II[5] and the possibility of their combination with radicals produced in the epoxy resin matrix by ionizing radiation is discussed. Polar-polar interactions, including hydrogen bonding formation, undoubtedly occur between the two phases. The polar-polar interaction between the two phases depends on the surface polarity of the component materials and, in turn, the polarity may change with ionizing radiation treatment.

The nature of interactions between two phases at the interface of composites has been examined by a number of investigators. However, no mechanisms or theories to date have fully explained the physical and chemical changes in epoxies, graphite fibers, or at the epoxy/fiber interface induced by radiation.

Here we extend our investigations of the molecular structural changes occurring in TGDDM-DDS epoxy upon exposure to high energy radiation[5-9] by examining the surface energetics of irradiated epoxy, graphite fiber and graphite fiber/epoxy composites to relate changes in mechanical properties of graphite fiber/epoxy composites[10-14] caused by exposure to high energy radiation. Polarity changes of the epoxy resin and graphite fiber after irradiation were studied using contact angle measurements, electron spectroscopy for chemical analysis (ESCA) and IR spectroscopy.

EXPERIMENTAL

Materials. The epoxy system examined in this study was MY 720 (Ciba-Geigy) based on tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) cured with 4,4'-diaminodiphenyl sulfone (DDS; Ciba-Geigy). Structures of the epoxy resin (TGDDM) and the hardener (DDS) are shown below:
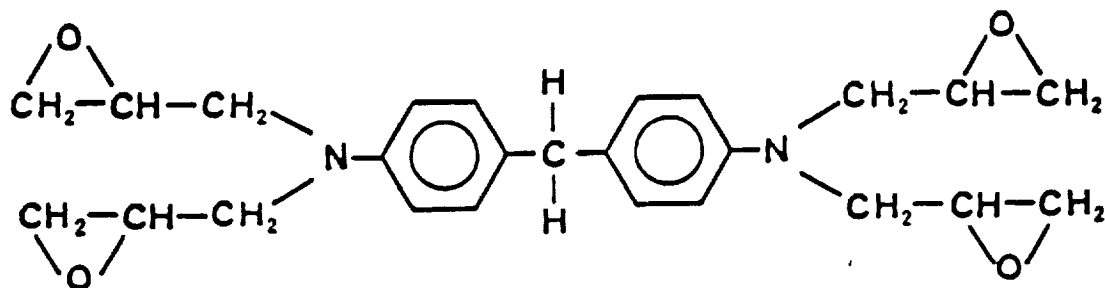
Tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM)
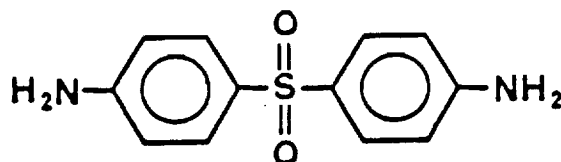
4,4'-diaminodiphenyl sulfone (DDS)

Both components were used as received without further purification. Hagnauer et al. have reported that pure TGDDM is the primary component of MY720 but that other species are present[15]. HPLC and GPC results from our laboratory confirm the presence of a small amount of oligomeric species in MY720 and that DDS is essentially pure[16].

T-300 (Union Carbide) graphite fibers without sizing treatment and a uniaxial composite of T-300 graphite fibers and NARMCO-5208 epoxy (T-300/5208) were used in the investigations of graphite fiber and composite samples, respectively.

Sample Preparation. A mixture of TGDDM/DDS (73/27 weight ratio) prepared as previously described[9] was placed between Teflon sheets with a Mylar® or aluminum foil spacer. The assembly was placed between stainless steel plates and then mounted in a Carver Press (110°C) and pressed slightly as the epoxy mixture melted to obtain a uniform film thickness. The mold was then clamped and immediately transferred into an oven which had been preset at 137°C. The temperature of the oven was then gradually raised to 150°C to avoid bubble formation in the cured film. The samples were cured at 150°C for 1 hr and then postcured at 177°C for an additional 5 hrs. Epoxy films of 25-250 μm (1-10 mil) thickness were obtained depending on the spacer thickness. For films <25 μm thick, no spacer was used. Cured samples were placed in air-filled Ziploc® bags, in nitrogen-filled Ziploc® bags, or in vacuum-sealed aluminum foil bags and then irradiated with 0.5 MeV electrons at ambient temperature. Irradiation of graphite fibers was made after the fibers had been spread as uniformly as possible between aluminum foil sheets.

Contact Angle Measurements. Contact angle measurements of the irradiated epoxy films and fracture surfaces from interlaminar shear tests of irradiated composite were made with an NRL goniometer (Rame-Hart). Contact angles for

graphite fibers were measured with a Cahn microbalance using the Whilemy technique. The specimens were washed with acetone and then with ethanol before contact angle measurements were made. An inclined angle of 10° was employed for contact angle measurements of the shear-fracture surface of the composite since no measurable sessile drop was formed in the horizontal position due to its surface roughness. The surface tension properties of test liquids were obtained from the literature[17].

IR Measurements: The IR spectra of the as-cured and the irradiated epoxy samples were measured on films that were ≈ 25 μm thick with a Perkins-Elmer Model 281B IR spectrometer. IR measurements of the uncured TGDDM/DDS mixture, pure TGDDM, DDS and DDM were obtained from a thin layer which had been cast on a KBr plate from acetone solution. Each sample on the KBr plate was dried under vacuum at room temperature until no trace of acetone was detected.

Electron Spectroscopy for Chemical Analysis (ESCA) Measurements. The relative oxygen to carbon content at the cured epoxy surface, graphite fiber surface, and the shear fracture surface of the composite was measured by ESCA before and after irradiation. Prior to ESCA measurements, the sample surfaces were washed with acetone and then with ethanol. All measurements were made with a Physical Electronics X-ray photo electron spectrometer located in the Chemistry Department at the University of North Carolina, Chapel Hill.

RESULTS AND DISCUSSION

Surface Energies of Irradiated Epoxy, Graphite Fiber, and Composites: The contact angles of liquids of varying surface tension on TGDDM-DDS epoxy irradiated with 0.5 MeV electrons at various dose levels at room temperature in nitrogen are listed in Table I. From the Young-Dupre equation, the work of adhesion W_a between the liquid and the solid surface may be calculated:

$$W_a = \gamma_L (1 + \cos\theta)$$

where γ_L is the surface tension of the test liquid and θ the measured contact angle. The polar ($\gamma_S P$) and dispersion ($\gamma_S d$) components of the total surface energy (γ_S) of the solid may be determined from the linear plot represented by the following equations[17].

$$W_a = \gamma_S + \gamma_L - \gamma_{SL}$$

$$\gamma_{SL} = (\alpha_S - \alpha_L)^2 + (\beta_S - \beta_L)^2$$

$$W_a/2\alpha_L = a_S + \beta_S(\beta_L/\alpha_L)$$

$$\text{where} \quad \alpha_S = (\gamma_S d)^{1/2} \qquad \alpha_L = (\gamma_L d)^{1/2}$$

$$\beta_S = (\gamma_S P)^{1/2} \qquad \beta_L = (\gamma_L P)^{1/2}$$

Figure 1 shows representative plots of $W_a/2\alpha_L$ vs β_L/α_L for TGDDM-DDS epoxy irradiated with various doses of 0.5 MeV electrons. Surface energy values estimated from Figure 1 as a function of radiation dose are plotted in Figure 2. The surface energy increases monotonically with radiation dose up to 1000 Mrad and then levels off. The total surface energy increase is mainly due to an increase in the polar component which must be caused by an increase in the number of polar groups on the surface of the epoxy. This result, in turn, is due to chemical changes produced by the ionizing radiation. As expected, the dispersion component remains almost constant.

Similar data for irradiation of the graphite fiber are in Table II and plotted in Figures 3 and 4. There is little change in surface energy of the fibers upon irradiation up to 10,000 Mrad though the polar component increases slightly (Table II). The change is not significant due to the stability of graphite to ionizing radiation and its high initial surface energy.

Contact angle changes with radiation for the composite fracture surfaces are shown in Table III. The data follow the same trends with radiation as the data for the epoxy samples. However, there is more variability in the contact angle measurements due to the surface roughness.

In order to examine the role of oxygen in the increase of polarity at the surface of the epoxy, as shown by the decrease in contact angles with H_2O (Table I), epoxy films were irradiated with 0.5 MeV electrons in air, nitrogen and under vacuum and their contact angles with H_2O were measured. The results are plotted in Figure 5. The contact angle decreases rapidly with dose for samples irradiated in air-filled or in nitrogen-filled Ziploc® bags, and decreases more slowly for samples irradiated in vacuum-sealed aluminum foil bags but eventually reaches approximately the same values as for the samples irradiated in air or nitrogen. This result indicates that oxygen is probably the most important factor determining the change in surface energy of the epoxy upon exposure to high energy radiation. The low contact angle value at the 1,000 Mrad dose level for condition (3) is probably due to oxygen diffusion into the vacuum-sealed aluminum-foil bag during irradiation.

Oxygen Content of Irradiated Surfaces: If the increase of surface energy with irradiation dose were due to the increase in polar groups produced mainly by oxidation, the oxygen content on the irradiated surface should increase upon irradiation. The same result can be expected for both outside surfaces and shear-fracture surfaces of the composite if dissolved oxygen is present.

A significant increase in oxygen content as measured by ESCA was observed on the irradiated epoxy surface (37% increase), irradiated graphite fiber (159% increase) and the fracture surface of the irradiated composite (51% increase) (see Table IV). As noted above, the contact angle of water on the fracture surface of the composite decreases upon irradiation (see Figure 5). This is con-

sistent with the increase in polarity of the epoxy surface and graphite fiber after irradiation. The increase of oxygen content at the fracture surface may indicate that oxidation reactions also occur at the interface of the composite upon irradiation. However, it should be noted that the oxidation of the fracture surface may also occur after the fracture surface is exposed to air since a high concentration of long-lived radicals is present in irradiated epoxy[5].

IR Spectroscopy: To examine the formation of functional groups which cause the increase in polarity of TGDDM-DDS epoxy upon irradiation, infrared (IR) absorption spectra of as-cured samples and those of irradiated samples were compared. IR spectra of individual components of MY720 and DDS were in agreement with those reported in the literature[18-20]. Figure 6 shows the effects of both curing and radiation on the carbonyl peaks at 1720 cm^{-1} and 1660 cm^{-1}. The absorption peak at 1720 cm^{-1} generally corresponds to aliphatic ketones or carboxylic carbonyls, and the peak at 1660 cm^{-1} corresponds to amides or aromatic carbonyl groups[21-23]. Since these carbonyl peaks are not present in the uncured TGDDM-DDS mixture (see Figure 7), the carbonyl groups in the unirradiated sample must be produced during the curing process, probably by oxidation due to the presence of dissolved oxygen. As the samples are irradiated, the intensity of the peak at 1720 cm^{-1} increases more than 110% at a dose level of 1,000 Mrad while that of 1660 cm^{-1} peak changes negligibly (<5%) (see spectrum 3 of Figure 7). Possible reaction schemes for the formation of carbonyl groups are discussed in part II.[5] Formation of carbonyl groups may occur during radiation with or without the presence of O_2, but the change in polarity on radiation even in samples under a N_2 blanket or under vacuum (Figure 5) suggests that dissolved oxygen plays a significant role.

CONCLUSIONS

The surface energy of both TGDDM-DDS epoxy increases monotonically with radiation dose up to about 1,000 Mrad mainly due to an increase in polarity. There is a small increase in the surface energy of graphite fiber with radiation. The polarity of the shear fracture surfaces of graphite fiber/TGDDM-DDS epoxy composites also increases with radiation dose. The oxygen content of the epoxy and the composite surfaces is shown by ESCA and IR spectroscopy to increase with radiation dose which accounts for the increase in the surface polarity. ESCA results on graphite fibers shows that there is a significant increase in the oxygen content with radiation dose. However, the high initial surface energy of the fiber results in small surface energy changes with radiation. The increasing polarity of the epoxy could be one reason for the increased interfacial strength of the composite upon irradiation (see references 11-14) due to increased polar-polar interactions.

ACKNOWLEDGEMENT

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Table I

Contact angle and Wa values for liquid/epoxy interface at various radiation doses (0.5 MeV electrons)

Liquid	Dose x 10^{-3} (Mrad)	Contact angle (degree)	Wa (ergs/cm^2)	$Wa/2\alpha_L$	β_L/α_L
Water	0	100.6	59.3	6.35	1.53
	0.4	72.0	95.2	18.20	
	1	25.0	138.8	14.90	
	2	27.2	137.6	14.73	
	5	26.3	138.1	14.79	
	10	13.5	143.6	15.37	
Ethylene glycol	0	70.9	64.1	5.92	0.81
	0.4	53.3	77.2	7.13	
	1	28.3	90.8	8.38	
	2	17.4	94.4	8.72	
	5	16.0	94.7	8.75	
	10	12.7	95.4	8.82	
Hexadecane	0	38.8	49.1	4.67	0.00
	0.4	23.3	52.9	5.03	
	1	13.3	54.5	5.19	
	2	6.8	55.0	5.24	
	5	4.7	55.1	5.25	
	10	4.8	55.1	5.25	

Table II. Contact angle and W_a values of graphite fiber versus radiation dose (0.5 MeV electrons)

Liquids	Dose x 10^{-3} (Mrad)	Contact Angle (degrees)	(erg/cm²) W_a	$W_a/2\alpha_L$	β_L/α_L
Water	0	38.6	129.7	13.89	1.53
	1	23.4	139.6	14.94	
	5	21.7	140.4	15.04	
	10	17.5	142.2	15.23	
Formamide	0	17.7	113.8	10.01	0.89
	1	18.4	113.6	9.99	
	5	9.7	115.8	10.18	
	10	16.5	114.2	10.04	
Ethylene-glycol	0	21.1	93.4	8.66	0.80
	1	15.2	94.8	8.76	
	5	10.6	95.8	8.84	
	10	19.6	93.8	8.66	
Tricresyl Phosphate	0	38.2	73.0	5.83	0.21
	1	30.6	76.1	6.08	
	5	36.5	73.8	5.89	
	10	28.3	81.1	6.14	
1-Bromo-naphthalene	0	30.2	88.2	6.60	0.00
	1	32.2	-	-	
	5	28.2	89.0	6.66	
	10	29.8	-	-	
Hexadecane	0	12.2	51.5	4.90	0.00
	1	-	50.9	4.85	
	5	4.9	51.9	4.94	
	10	-	51.6	4.91	
Hexane	0	10.1	36.5	4.26	0.00
	1	-	-	-	
	5	0.0	36.8	4.29	
	10	-	-	-	

Table III.

Contact angles (degree) of water on shear-fracture surface and outermost surface of T300/5208 uniaxial composites irradiated with 0.5 MeV electrons in vacuum-sealed aluminium-foil bags.

	Contact Angles	
	Control	7,500 Mrad
Fracture Surface		
Fiber Direction		
Advancing	61.7	45.2
Receding	-	-
Lateral Direction		
Advancing	85.0	59.0
Receding	84.0	59.0
Outermost Surface		
Advancing	88.0	54.3
Receding	83.3	53.6

Table IV

Relative atomic concentration of oxygen (0) to carbon (C) on TGDDM-DDS epoxy, graphite fiber and fracture surfaces of T300/5208 composite as determined by ESCA.

Sample	O/C	%increase in oxygen compared to control
Epoxy		
As-cured	0.237	
10,000 Mrad	0.324	37%
Graphite Fiber (T-300)		
Control	0.191	
10,000 Mrad	0.494	159%
Composite (Fracture Surface)		
Control	0.237	
10,000 Mrad	0.358	51%

LIST OF FIGURES

EPOXY (TGDDM - DDS)

Figure **J**   Plot of $W_a/2\alpha_L$ against β_L/α_L of TGDDM-DDS epoxy. Samples were irradiated with 1/2 MeV electrons at room temperature.
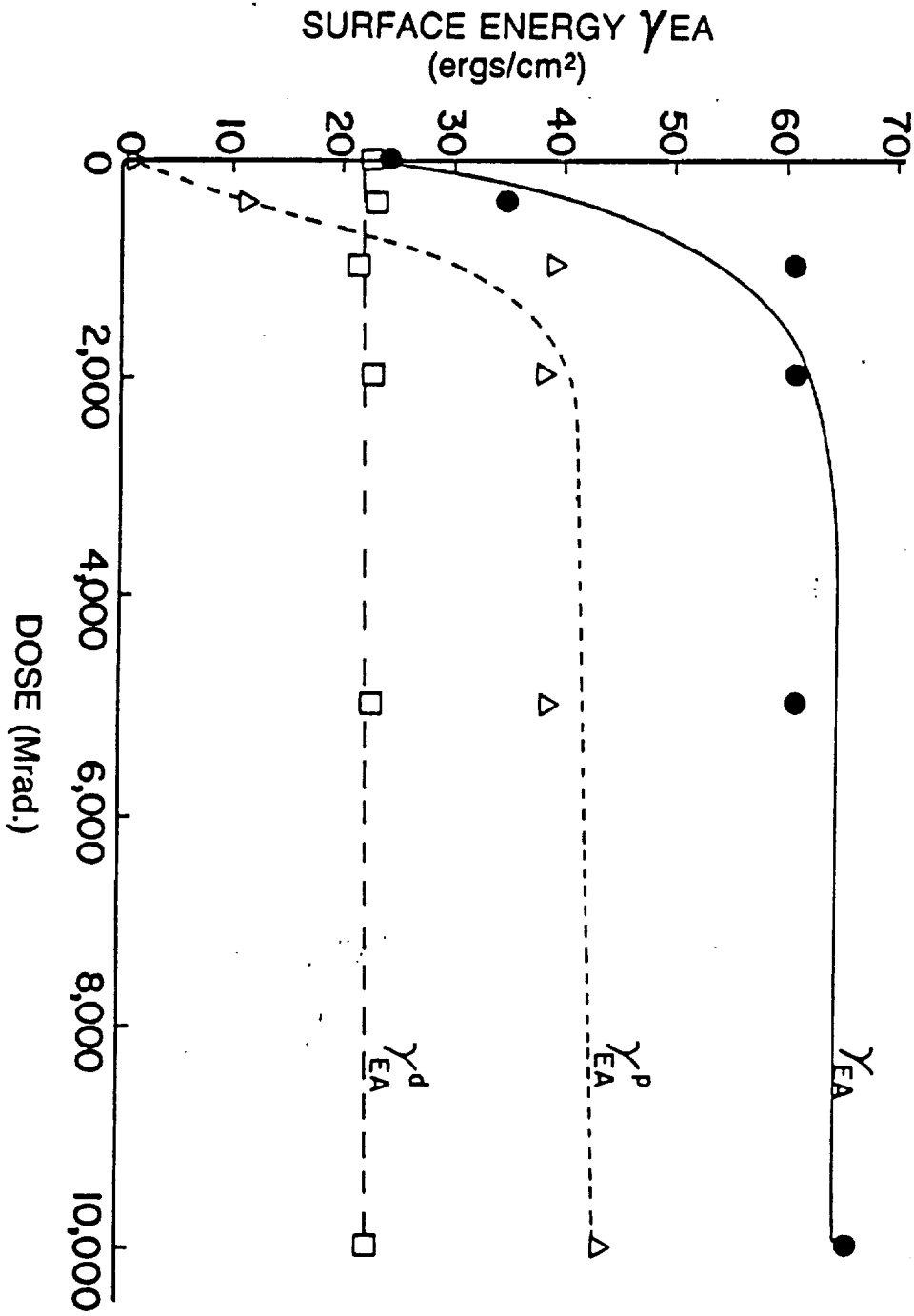
Figure 2. Surface energy changes of TGDDM-DDS epoxy with radiation dose.
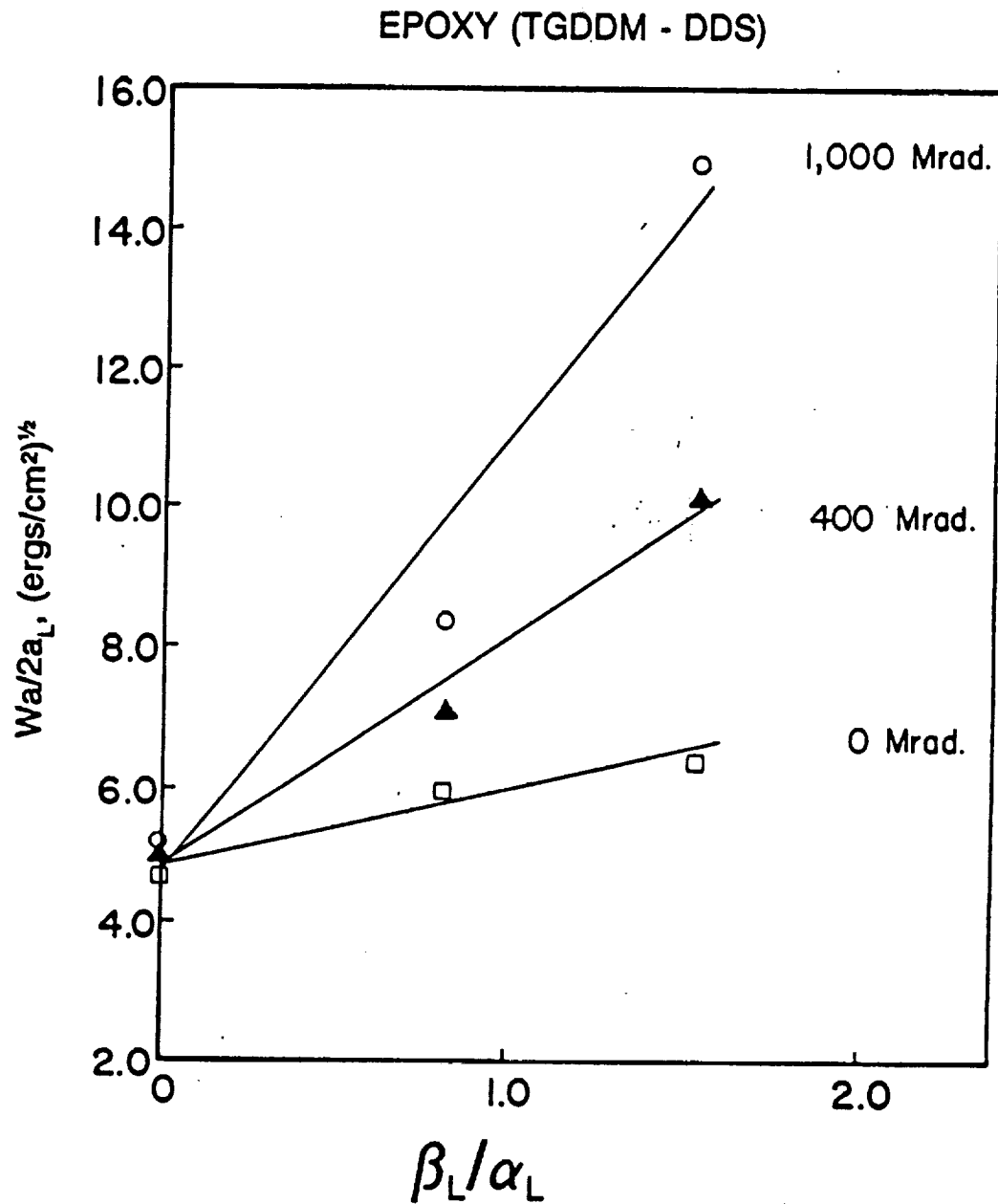
GRAPHITE FIBER

Figure 3 Plot of $W_a/2a_L$ against β_L/α_L of T-300 graphite fiber. Samples were irradiated with 1/2 MeV electrons at room temperature.

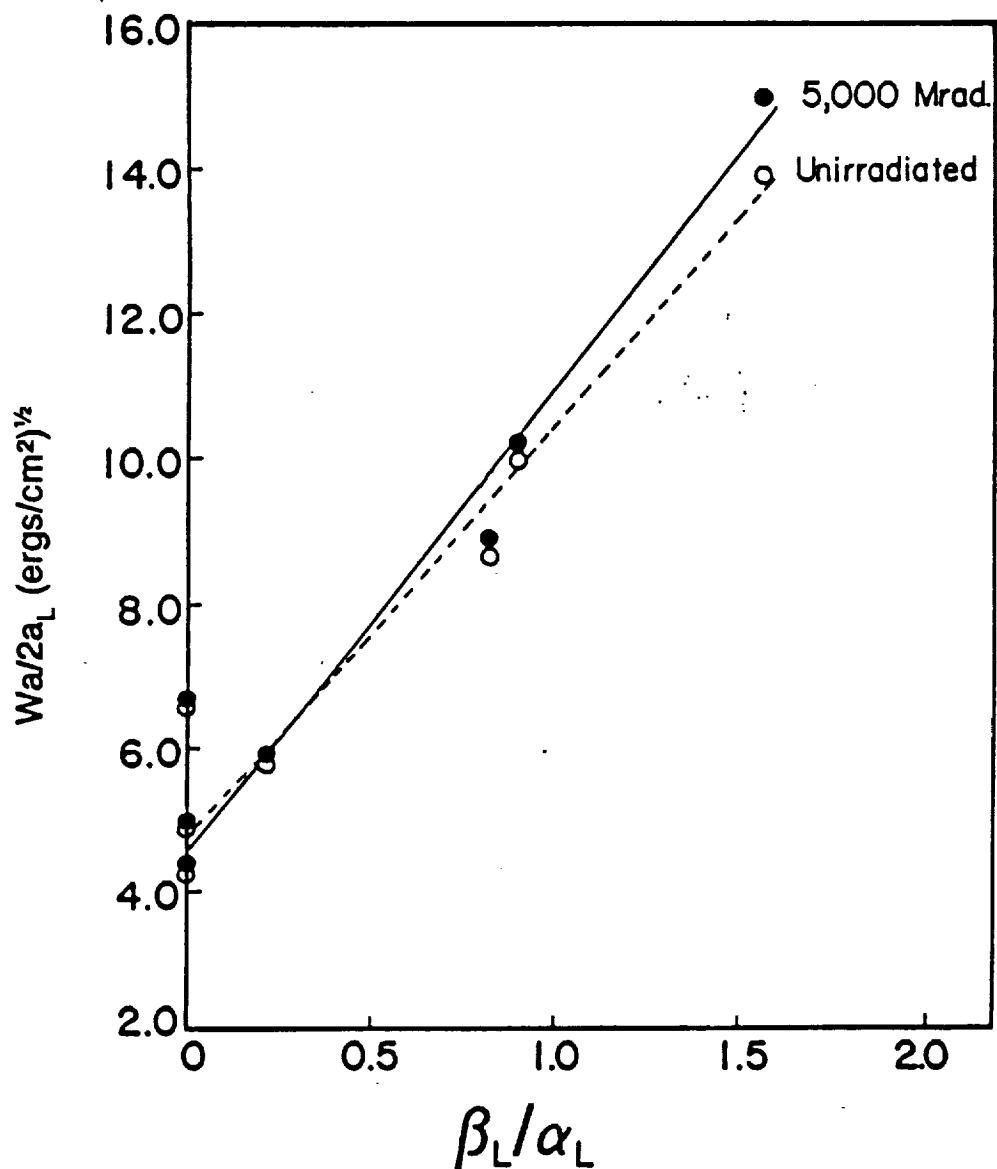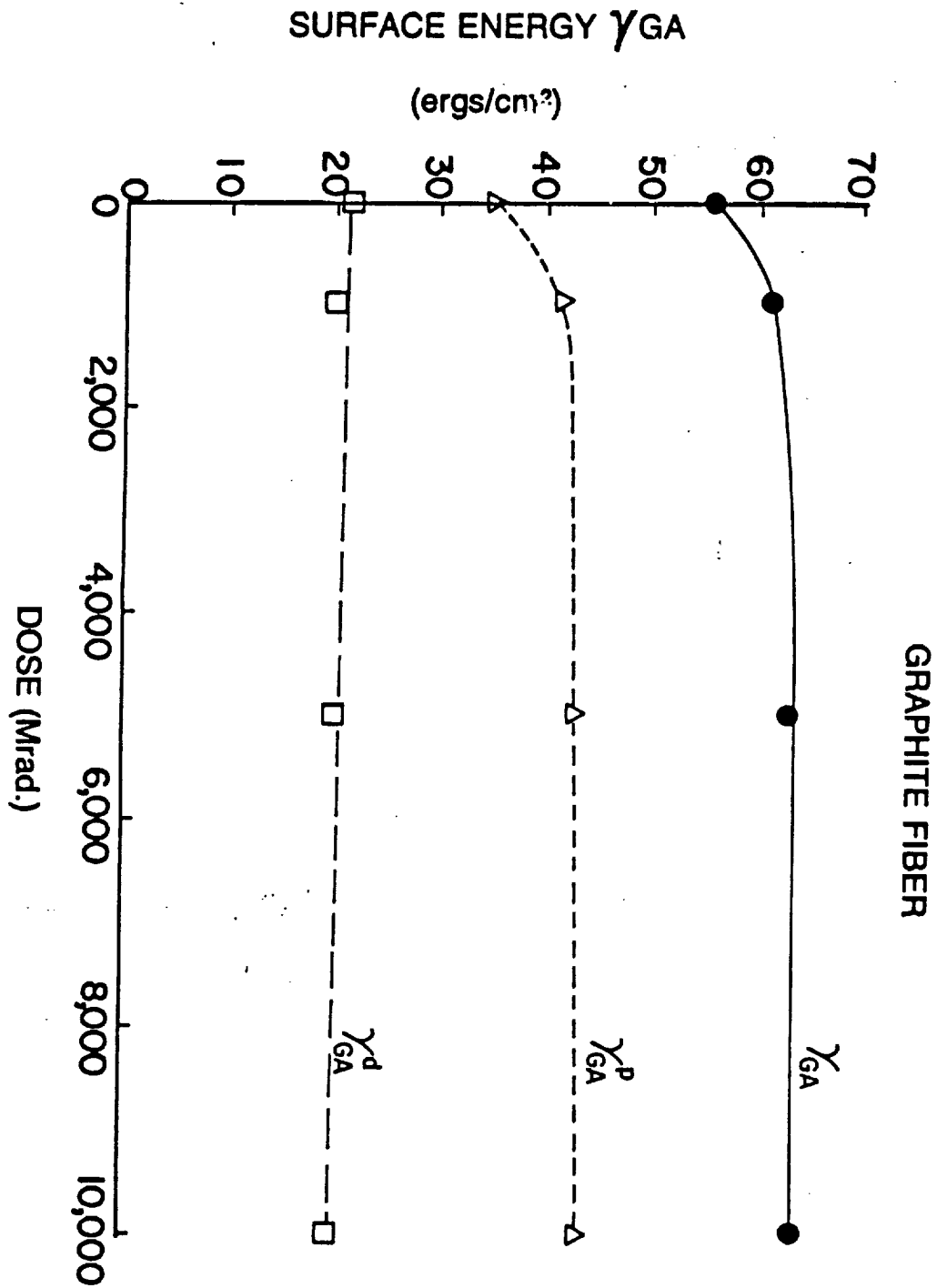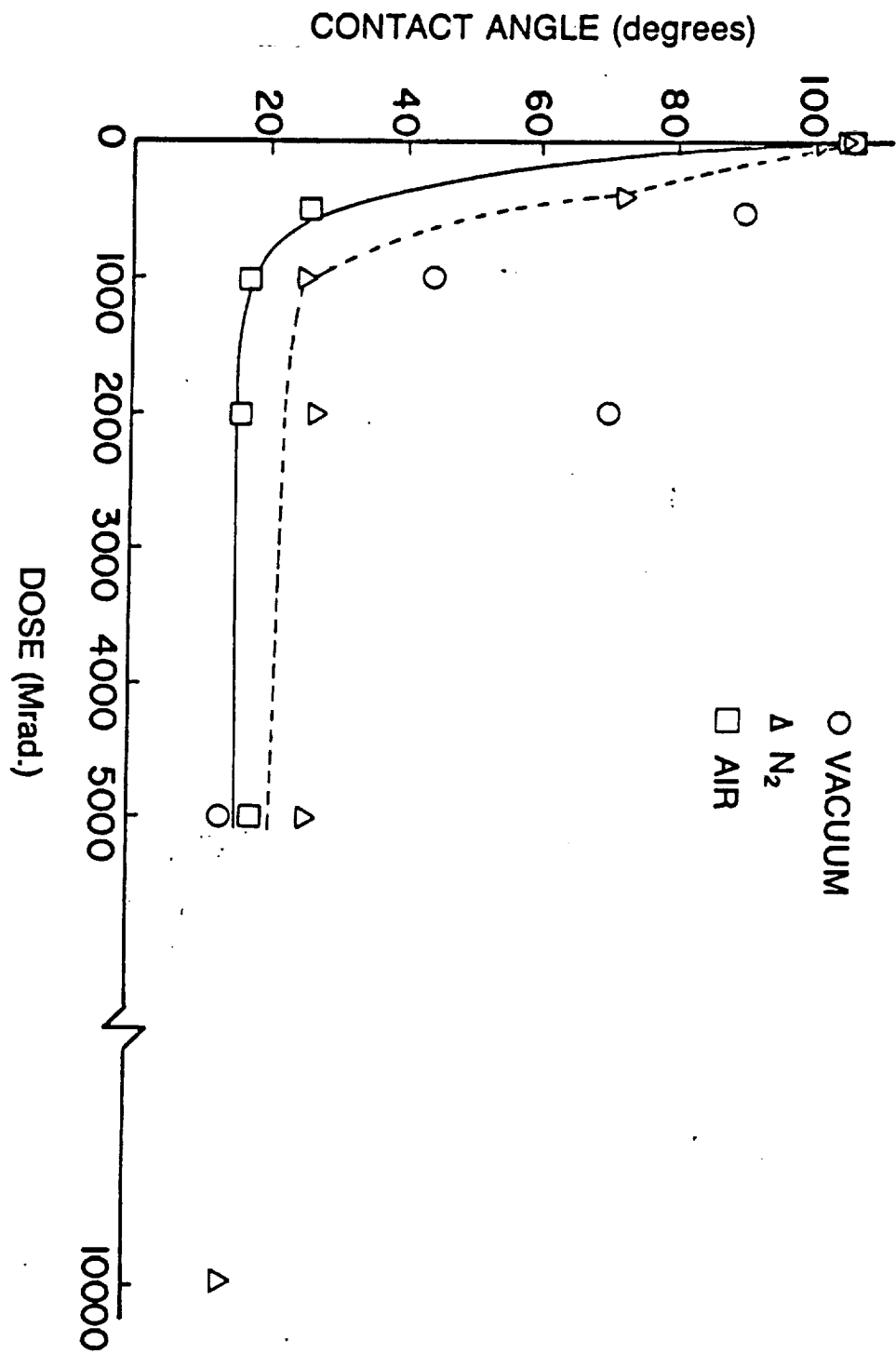Figure 4 Surface energy changes of T-300 graphite fiber with radiation dose.
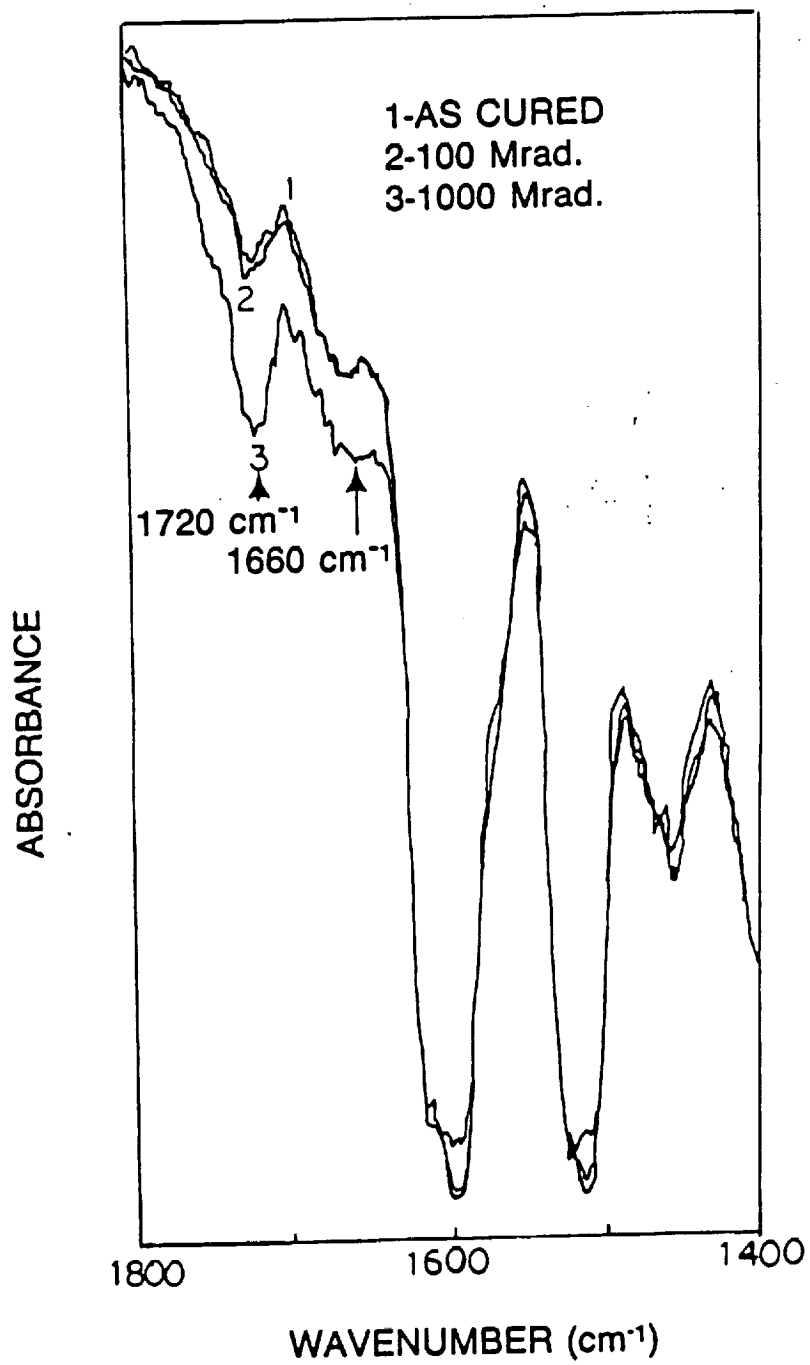
Fig 5

CONTACT ANGLE (degrees)

DOSE (Mrad.)

○ VACUUM
△ N₂
□ AIR

Fig 6
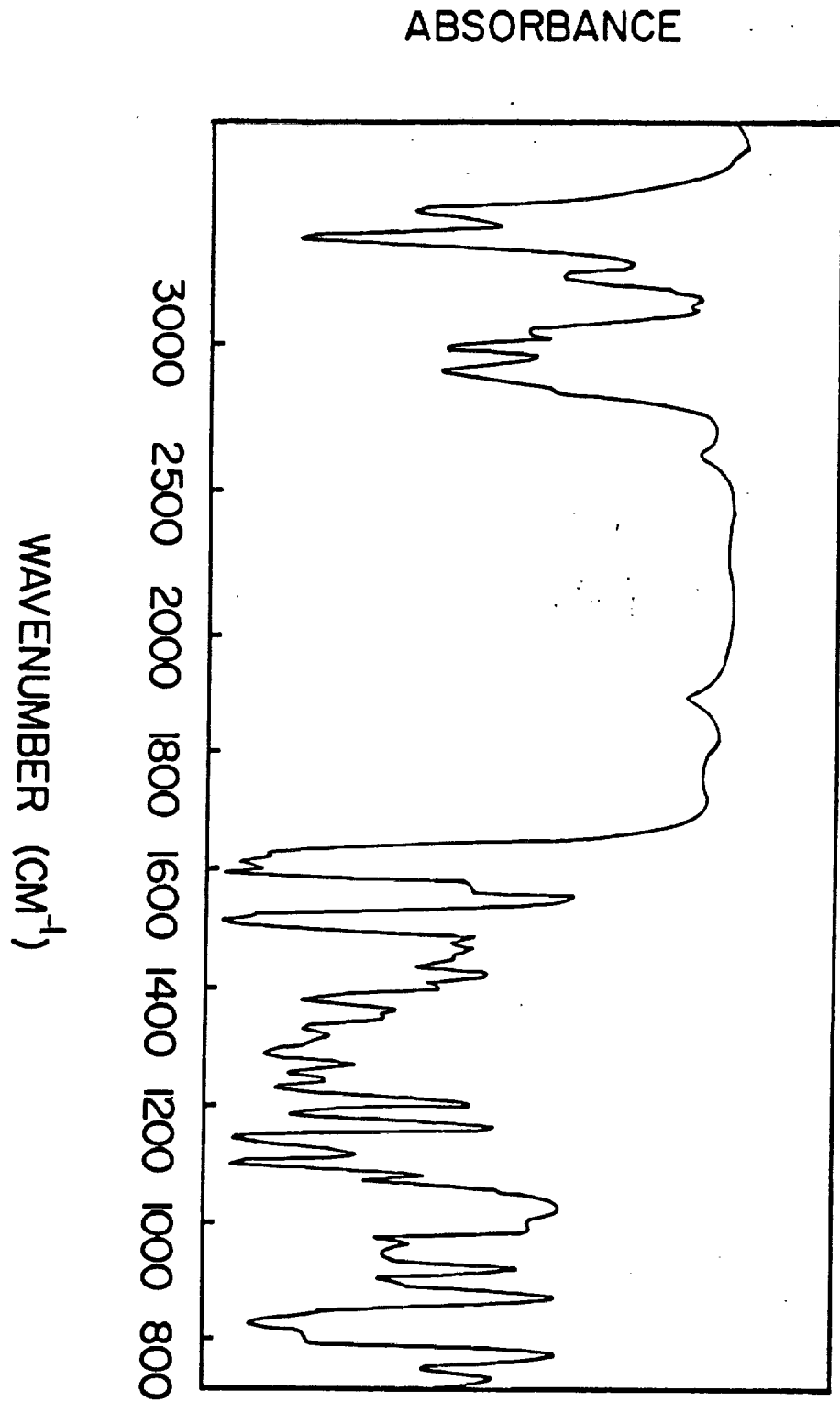
Figure 7 IR spectrum of the as-mixed TGDDM-DDS.

Effects of Ionizing Radiation on Epoxy, Graphite Fiber and Epoxy/Graphite Fiber Composites

Part II: Radical Types and Radical Decay Behavior

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Synopsis

Electron spin resonance (ESR) investigations of line shapes and the radical decay behavior have been made of an epoxy based on tetraglycidyl diaminodiphenyl methane (TGDDM)/diaminodiphenyl sulfone (DDS), T-300 graphite fiber, and T-300/5208 (graphite fiber/epoxy) composites after irradiation with Co^{60} γ-radiation or 0.5 MeV electrons. Two kinetically distinct radical species are found in the irradiated epoxy as the temperature is raised beyond $120^{\circ}K$ following irradiation of samples at $77^{\circ}K$ with $Co^{60}\gamma$. One has been termed a fast-decaying species and the other a slow-decaying species. The ratio of fast-decaying/slow-decaying radicals increases as the decay temperature rises. The fast-decaying radicals at room temperature are attributed largely to alkyl type radicals residing in regions of relatively low crosslink density while the long-lived radicals are attributed to radicals residing in the highly-crosslinked regions of the epoxy. A large concentration (ca.

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$10^{20} - 10^{21}$ spins/g) of unpaired electrons was found in unirradiated graphite fiber which masked the ESR spectral change in irradiated composites.

INTRODUCTION

High performance fiber/polymer composite materials are widely used today in aerospace technology because of their superior properties such as high strength/weight ratio and dimensional stability. In a 20-30 years space operation in the geosynchronous orbit, for example, the materials may be exposed to ionizing radiation such as electrons, protons and γ-radiation in addition to ultra violet light with doses up to 10,000 Mrad.[1-2] Under such long-term space operations, the mechanical integrity of composite materials, especially interfacial strength between the fiber and the matrix is of prime importance. Diverse mechanisms have been proposed in the literature for the radiation-induced degradation or oxidation of epoxies, particularly those based on the diglycidyl ether of bisphenol A (DGEBA). However, there are few studies of the epoxy based on tetraglycidyl diaminodiphenyl methane (TGDDM) cured with diaminodiphenyl sulfone (DDS), an epoxy which is widely used today in high performance composites.

In earlier work on TGDDM/DDS - graphite fiber composites, it was shown that flexural strengths and moduli based on three point bending tests increased with radiation[3,4]. Park et. al.[5] demonstrated the interlaminar shear strength of this system increases after long exposure (10,000 Mrad) to ionizing radiation. In this paper we report on investigations of radical concentration, types and decay properties of the free radicals produced in TGDDM/DDS epoxy and epoxy/graphite fiber composites exposed to ionizing radiation. The main objective is to relate molecular structural changes of TGDDM-DDS epoxy and T-300 graphite fiber due to ionizing radiation to mechanical property changes occurring in graphite fiber/epoxy composites under the same conditions.

EXPERIMENTAL

Materials. The epoxy system examined in this study was MY 720 (Ciba-Geigy) based on tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) cured with 4,4'-diaminodiphenyl sulfone (DDS). Both were obtained from Ciba-Geigy and used without further purification. Structures of the epoxy resin (TGDDM) and the hardener (DDS) are shown in earlier work[6]. The TGDDM and DDS (73/27 weight ratio) were thoroughly mixed at 110^0C. The molten TGDDM/DDS mixture was sucked into a 2.4-mm ID Teflon® tube using an aspirator and then cured under various conditions with both ends of the tube sealed with Teflon® tape. Cylindrical rods with 2.4 mm diameter x 3 cm length were cut from the cured rods and used as the samples for ESR spectroscopy. T-300 (Union Carbide) graphite fiber without sizing treatment and a uniaxial composite of T-300 graphite fiber and NARMCO-5208 epoxy (T-300/5208) were used for the graphite fiber and composite samples, respectively.

Irradiation. Co^{60} γ-radiation exposures were carried out either at room temperature or at 77^0K in liquid nitrogen while the 0.5 MeV electron exposures were made at room temperature. The composite samples were irradiated in vacuum-sealed aluminum foil bags. The graphite fibers were spread between aluminum foil sheets and irradiated in air with electrons.

ESR Measurements. All ESR measurements were carried out on a JEOL JEX-ME-1X ESR spectrometer. Measurements were made on a bundle (1-2 mg) of parallel graphite fibers that were inserted in a 2.4 mm ID x 3 cm length Teflon® tube and placed in the ESR tubes. ESR measurements of T-300/5208 composites were made on strips that were approximately 0.5 mm x 2.5 mm x 3 cm split from composite coupons. The radical concentration of a sample was determined by comparing the spectral area of the sample and that of a standard prepared in the same geometry by mixing 2,2-diphenyl-1-piycrylhydrazyl (DPPH) with a commercial
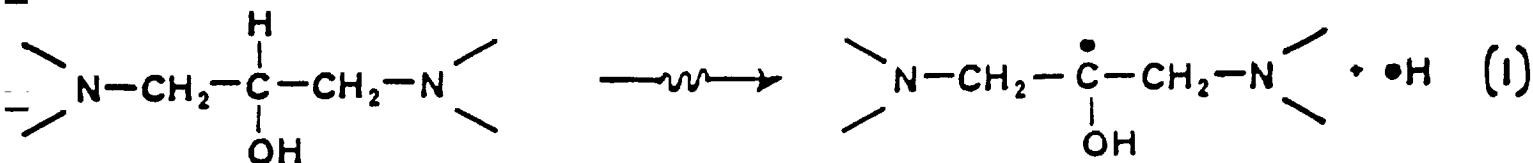
epoxy glue (Elmers®). The spectral area was determined from graphical double-integration of the first derivative ESR spectrum (see reference 7).
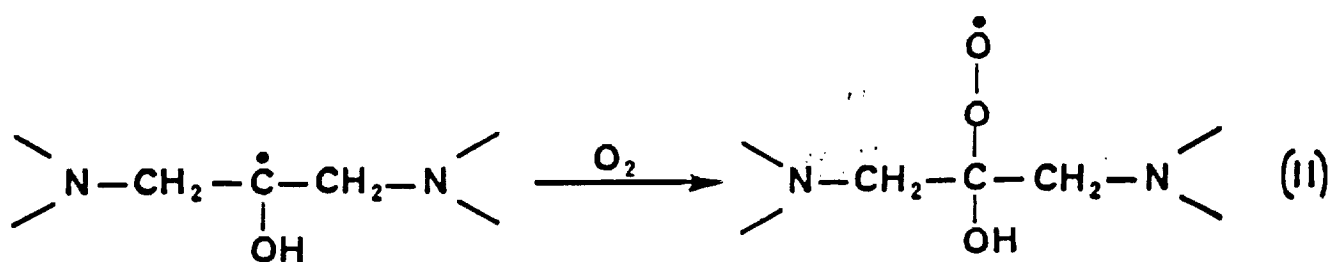
RESULTS AND DISCUSSION

Epoxy ESR Line Shapes: ESR spectra of epoxy irradiated with γ-radiation at $77^\circ K$ in liquid N_2 and in air at room temperature are shown in Figures 1. The latter has a more intense, narrow component compared to the former with a peak-to-peak width (ΔHpp) of ca. 13 gauss (G). This narrow component decays faster than the other component and the overall line shape becomes asymmetric when the irradiated sample is exposed to room temperature in the air. Also it does not have long tails which are observed in the epoxy irradiated at $77^\circ K$. The long tail observed in the spectrum of one of the former samples disappears rapidly, within five minutes, after the irradiated sample is warmed up to room temperature, and the spectrum become a relatively symmetric broad singlet ($\Delta Hpp = 22\text{-}25$ G). For the room temperature irradiated samples, such long tails associated with fast-decaying species are not observed since they may decay during irradiation. This assumption is supported by the fact that the radical concentration in a sample irradiated at room temperature is lower (ca. 0.5×10^{19} spins/g) than that for a sample irradiated at $77^\circ K$ (ca. 2.5×10^{19} spins/g.) with the same dose. A sample irradiated with 0.5 MeV electrons has a similar spectrum to that of a room temperature γ-irradiated sample.

The additional narrow ESR component in a room temperature irradiated sample clearly indicates that different radical species are produced depending on the irradiation conditions. For the case of $77^\circ K$-irradiation, liquid nitrogen protects the sample from external oxygen. Also all radicals are presumed to be unreactive at this low temperature. At room temperature in air, on the other hand, some of the radicals probably react with oxygen which undoubtedly is

present in the samples[6]. Also, some radicals may have sufficient mobility at

room temperature to undergo recombination during irradiation. In order to exa-

mine the effect of oxygen, a sample was vacuum-sealed in an ESR tube and γ-

irradiated at room temperature with a dose of 800 Mrad. As seen in Figure 2,

the narrow component in the ESR line still appears and only a slight increase

in intensity is noticed compared to the sample irradiated in air. Even with con-

tinuous pumping (with a rotary vacuum pump) during irradiation the narrow ESR

component appears when a sample is irradiated at room temperature. Dissolved

oxygen, which may not be completely removed even under the continuous vacuum

treatment (due to the low diffusivity of oxygen in the epoxy) may cause oxidation

reactions which would eventually lead to chain-scission reactions. Possible

chain-scission reactions in TGDDM-DDS epoxy under ionizing radiation in the pre-

sence of oxygen are suggested below following the general photooxidation

mechanism[8-9].

$$
\text{>N-CH}_2\text{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}\text{-CH}_2\text{-N<} \quad \xrightarrow{\text{\scriptsize$\mathord\sim\!\!\sim$}} \quad \text{>N-CH}_2\text{-}\underset{\underset{OH}{|}}{\overset{\bullet}{C}}\text{-CH}_2\text{-N<} \; \cdot \; \bullet H \quad (1)
$$

$$\diagdown \!\! N - CH_2 - \overset{\bullet}{\underset{\underset{OH}{|}}{C}} - CH_2 - N \!\! \diagup \xrightarrow{\quad O_2 \quad} \diagdown \!\! N - CH_2 - \underset{\underset{OH}{|}}{\overset{\overset{\overset{\bullet}{O}}{\underset{|}{O}}}{C}} - CH_2 - N \!\! \diagup \qquad (II)$$

The peroxy radical may abstract hydrogen from other molecules or react with the hydrogen from reaction (I):
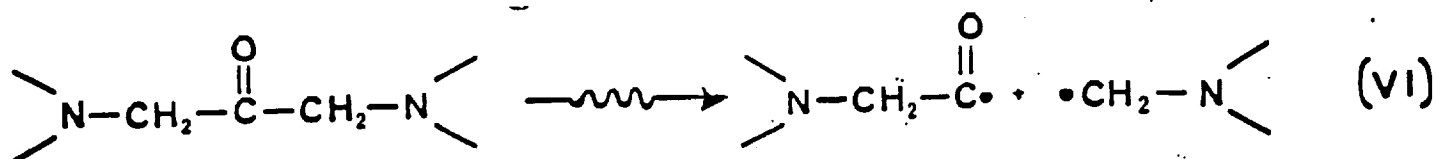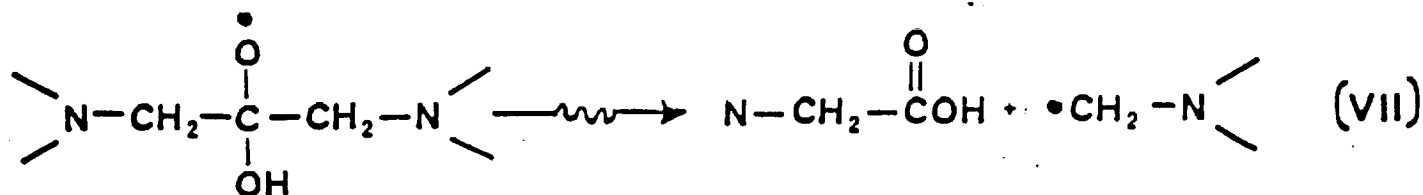
(III)

(IV)

(V)
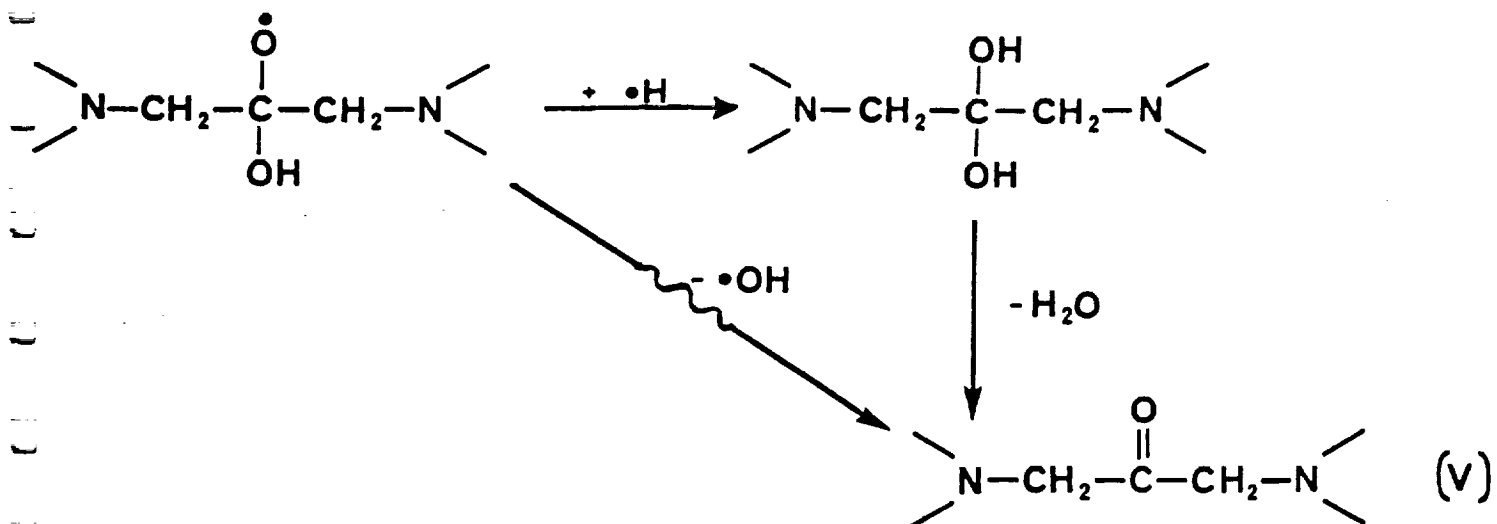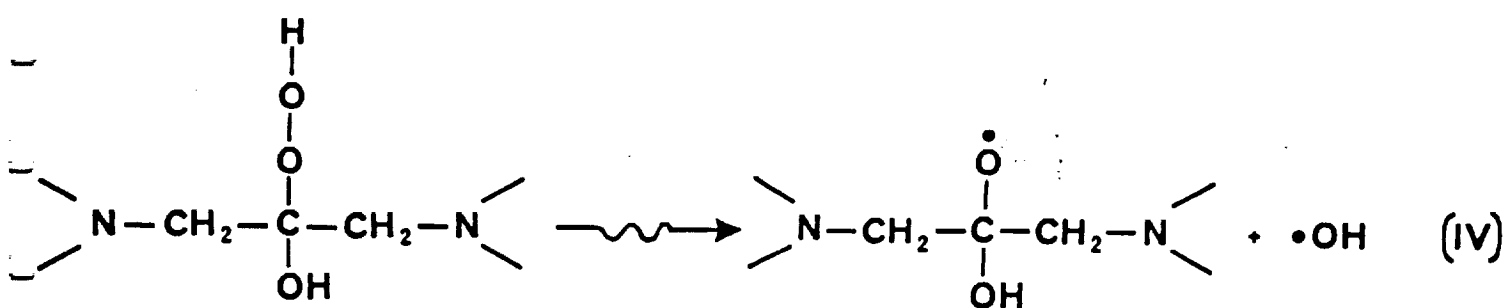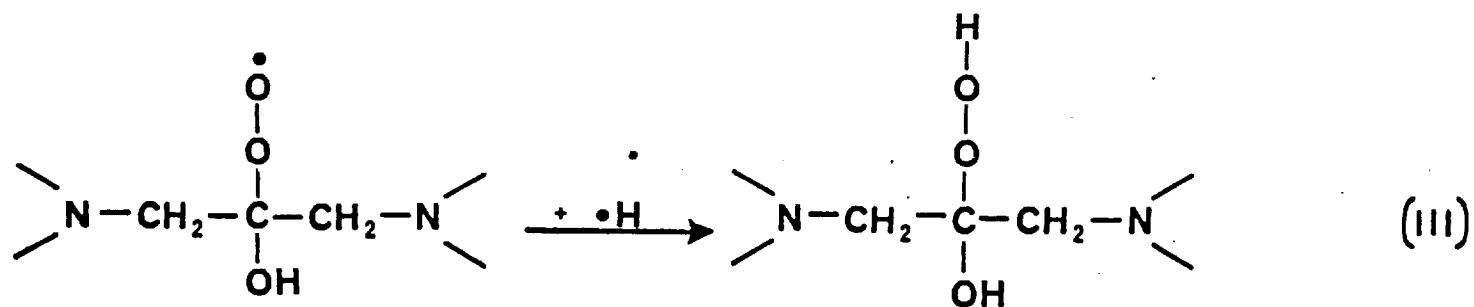
With further irradiation, the ketone of reaction (V) undergoes a Norrish Type I reaction resulting in chain-scission:

$$\underset{\diagdown}{\diagup} N-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-N \overset{\diagup}{\diagdown} \quad \longrightarrow \quad \underset{\diagup}{\diagdown} N-CH_2-\overset{\overset{O}{\|}}{C}\bullet \; + \; \bullet CH_2-N \overset{\diagup}{\diagdown} \qquad (VI)$$

Chain-scission may also occur directly from the alkoxy radicals of reaction (IV):

$$\underset{\diagup}{\diagdown} N-CH_2-\overset{\overset{\bullet O}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-N \overset{\diagup}{\diagdown} \quad \longrightarrow \quad N-CH_2-\overset{\overset{O}{\|}}{C}OH \; + \; \bullet CH_2-N \overset{\diagup}{\diagdown} \qquad (VII)$$

or from the alkyl radicals of reaction (I) in the absence of oxygen through the following reaction:

$$\underset{\diagup}{\diagdown} N-CH_2-\overset{\overset{\bullet}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-N \overset{\diagup}{\diagdown} \quad \longrightarrow \quad \underset{\diagup}{\diagdown} N-\overset{\bullet}{C}H_2 \; + \; \overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}=CH-N \overset{\diagup}{\diagdown} \qquad (VIII)$$
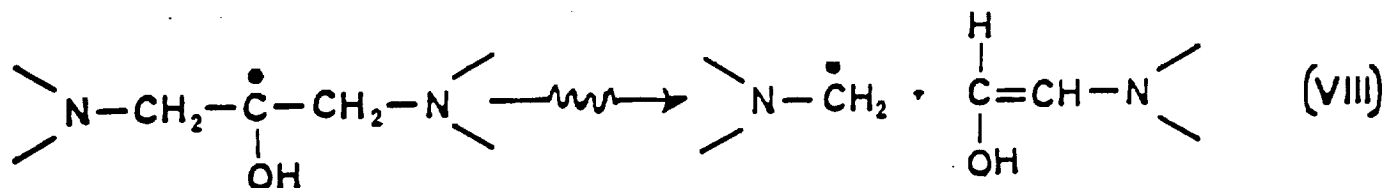
When samples are irradiated at room temperature, the alkyl radicals produced through reactions (I), (VI), (VII), and (VIII) may react rapidly during irradiation and thus may be reduced in concentration at the time the ESR measurement is made. On the other hand, the acyl radicals produced through reaction (VI) are expected to be relatively stable compared to the alkyl radicals. The former should be more mobile than other oxygenated radicals which reside along the main chains and therefore could be detected as a more narrow ESR component. Tsuji et al.[10] and Noda et al.[11] have reported narrow ESR lines with ΔHpp ranging 12-20 G in irradiated polyethylene and acyl chlorides, respectively, and assigned the narrow singlets to acyl type radicals. The observed line width

of approximately 13 G for the narrow component in the present study is also comparable to the 16.6 G line width which has been calculated by Gupta et al.[12] for acyl type radicals in irradiated TGDDM-DDS epoxy.

Figure 3 shows the ESR line shape changes with time of slightly irradiated epoxy samples. When a sample irradiated at 77°K is warmed up to room temperature, the long tails disappear within 5 minutes and the spectrum becomes a broad singlet (ΔHpp = 22-25 G). These results are consistent with earlier studies by Kent et al[7] and Schaffer et al[13]. The difference spectrum (see Figure 4) generated by subtracting the spectrum after 5 minutes decay at room temperature (Figure 3b) from the as-irradiated spectrum (Figure 3a) has a quintet-like line shape. This can be interpreted as a composite spectrum of several different lines from different radical species. As alkyl type radicals are quite reactive,[8,14-15] this difference spectrum, which corresponds to the fast-decaying fraction of the spectrum, may be attributed mostly to alkyl type radicals such as $-CH_2-\overset{\bullet}{C}-CH_2-$

$$\begin{array}{c} OH \\ | \end{array}$$

along the main chain, or $\cdot CH_2$ and/or $-\overset{|}{\underset{|}{C}}\cdot$ produced by main-chain scission.
$$\begin{array}{c} | \\ H \end{array}$$

The broad singlet spectrum (see Figures 1b) observed for 77°K-irradiated samples after prolonged times (e.g., for 200 minutes) in air at room temperature are due to stable radical species probably residing in highly crosslinked regions of the epoxy network. A similar broad line (ΔHpp = 22-25 G) is also observed for as-cured (i.e. unirradiated) epoxy samples. The concentration of these thermally produced radicals is in the range of 0.2 - 0.7 x 10^{18} spins/g and increases slightly with curing time and curing temperature. Similar spin concentrations and line widths have been reported by several authors.[7,13,16] Coulter et al.[16] have suggested that the singlet spectrum of the

as-cured epoxy is due to alkyl radicals ($-CH_2-\overset{\bullet}{\underset{|}{C}}-CH_2-$) which result from loss of a

tertiary hydrogen from the carbon of alkyl side chains in TGDDM. Since alkyl

radicals are characteristically reactive, they may eventually transform into less

reactive oxygenated radicals by reacting with dissolved oxygen or oxygen that

diffuses into the sample resulting in alkoxy ($-\overset{|}{\underset{|}{C}}-O\cdot$) or peroxy ($-\overset{|}{\underset{|}{C}}-OO\cdot$) radi-

cals. The results reported in part I[6] clearly show that oxygen is involved in

reactions of this system when it is exposed to ionizing radiation.

Radical Reactions and Decay: The rate of radical reaction and consequently

radical decay in polymeric materials is associated not only with radical types,

but also with the mobility of polymer radicals and the diffusivity of gases

produced by irradiation. In turn, the mobility of radicals and diffusivity of

gases are primarily controlled by the physical state (crystallinity or crosslink

density) of polymers where the radicals reside. As a result, the overall radi-

cal decay kinetics in an irradiated epoxy which has a characteristically inhomo-

geneous network structure can be very complex as in the case of semicrystalline

polymers.

Figure 5 shows the isothermal decay of the radical concentration of an

TGDDM-DDS epoxy following exposure to γ-radiation at 77°K. In each case there

is an initial fast decay followed by a much slower rate of decay. Similar radi-

cal decay behavior at room temperature of the same epoxy has been reported by

Kent et al[7] and Schaffer et al[13]. As the temperature of the irradiated samples

is increased, a greater fraction of total radicals decay out at the early stage.

Although the overall decay reaction does not follow any simple kinetic rule, the

half lives of the fast-decaying and slow-decaying species at room temperature

estimated from the first order plot are approximately 3.5 minutes and 600 minu-

tes, respectively. The initial fast-decaying radicals are attributed primarily

to reactive radicals, including alkyl radicals, that reside in low-crosslinked

regions or voids in the cured epoxy. The available hydrogen and trapped free electrons near reaction sites will be depleted quickly and radicals which are mobile enough to recombine will also disappear in the early stage. Thereafter, changes in the radical concentration occur more slowly due to the lack of reactive gases and decreased concentration of available radicals to react, i.e. decreased probability of recombination. The hydrogen hopping mechanism through which radicals become close to each other for recombination may play an important role in this later stage. As the temperature rises, additional radicals which have been trapped in intermediate crosslinked regions may acquire enough energy to react and disappear during the early stage. Since all the isothermal radical decay measurements were made at temperatures below the glass temperature of the epoxy system (Tg $\cong$ 200°C), the increase of the temperature should not affect significantly the decay rate constant of the long-lived radicals in the highly crosslinked or immobile regions.

The effects of crosslinking density on radical decay behavior of irradiated epoxy were further examined as a function of curing temperature, curing time, and radiation dose. It is known that as the curing temperature increases the extent of crosslinking of an epoxy system increases[17-19]. Once the epoxy system reaches the vitrification point, further extension of the curing time at a given cure temperature does not significantly increase the extent of reaction due to the lack of diffusional transport of reactive sites such as secondary amines. Crosslinking at this stage occurs mainly through the formation of ether linkages by the reaction between hydroxyl and epoxy groups. Further reaction of the secondary amine occurs only when the curing temperature becomes higher than the glass transition temperature of the "on-curing system".[20] The concentration of the long-lived radical species trapped in the irradiated epoxy increases with curing temperature which again is attributed to increased crosslink density. The effect of the curing time on the radical concentration is not strong. The low

dependency of the concentration of the long-lived radicals on curing time may be due to the relatively low maximum cure temperature (160°C/employed) and the short time required for vitrification, a result that is consistent with other work.[20] The variation in initial radical concentration of samples irradiated to the same dose level but cured under different conditions is probably due to an uncertain elapse of time (< 1 minute) involved during transferring the sample from the liquid nitrogen to the ESR cavity.

The effect of radiation dose levels on the radical decay behavior in the epoxy was also examined in this study. The concentration of long-lived radicals increases with radiation dose and is approximately proportional to radiation dose (at doses less than 100 Mrad). This result is consistent with previous studies[7,13]. Also, the cured epoxy contains unreacted functional groups since 100% reaction is not generally achieved for various reasons such as lack of mobility of reactive sites[17,20-21]. The unreacted sites will undergo additional curing reaction upon exposure to high energy radiation[21]. However, the dose levels here are not sufficiently high to affect significantly the average crosslinking density.

ESR Spectra of Graphite Fiber and Composites: The ESR spectra of T-300 graphite fiber and an epoxy/graphite fiber composite (T300/5208) irradiated with 0.5 MeV electrons at room temperature are shown in Figure 6. Both line shapes are similar and both are singlets. The same line shapes were observed for the unirradiated graphite fiber and composite samples. The line width (ΔHpp) of the singlet for graphite fiber is about 4 G. Its g-factor is 2.0023 which is close to that of free electrons. The ESR line width (ΔHpp) and the g-factor of the composite are about 5 G and 2.000 ± 0.001, respectively. The slight differences in the line width and the g-factor between the graphite fiber and the composite are probably due to different environments in which the unpaired electrons are

residing. The ESR signal observed in the crystalline graphite has generally an asymmetric line shape which is often attributed to conduction electrons[22-23]. However, the singlet observed in the present study is symmetric and very much like the ESR line shape found in carbon blacks or carbon fibers which contain a large concentration of radicals associated with pyrolysis[24]. It did not show a power saturation which is usually observed for free electrons, when the microwave power is about 2 mW. If the observed singlet in the graphite fiber or composites is associated with free radicals, there may exist a chemical interaction between radicals in the graphite fiber and the radicals in the epoxy at the interface. In some cases, the unpaired electrons just beneath the surface of the graphite fiber may migrate to the interface and experience a variation in their electron environments as in the case of the carbon black/rubber interface[25]. We were unable to resolve any ESR spectral change after irradiation of the graphite fiber and the composite because unirradiated graphite fibers contain a large spin concentration ($\sim 10^{20}$ - 10^{21} spins/g.), which is approximately two orders of magnitude higher than the concentration in the epoxy irradiated with a dose of over 1,000 Mrad of 0.5 MeV electrons (10^{19} spins/g). The spin concentration measured in an unirradiated composite is of the same order of magnitude as in the unirradiated graphite fiber, and the background overshadows possible spectral change in the composite as a result of irradiation.

If unpaired electrons in the graphite fiber eventually interact with free radicals produced in the irradiated epoxy at the fiber/epoxy interface (for example, through formation of chemical bonds or chemisorption of radicals), then this may account for the enhancement of the bond-strength of the composite after irradiation, as observed by many authors[2-5]. If there were such chemical reaction between the radicals in the graphite fiber and those produced in the epoxy by radiation, then the radical concentration of the composite should change

after irradiation. No confirmation of the reaction between radicals in the epoxy and those in the fiber was made in the present study. Although the exact nature of the reaction between radicals (unpaired electrons) in the graphite fiber and those generated in the epoxy by irradiation has not been reported, chemical bond formation or chemisorption between polymer radicals may occur across the interface of composites. This is similar to phenomenon that have been suggested by several authors[25-28] to occur between radicals in rubber and on the surface of carbon black.

CONCLUSIONS

Electron spin resonance (ESR) spectra of TGDDM-DDS epoxy irradiated at liquid nitrogen temperature ($77°K$) with γ-radiation has two main components, one with very broad shoulders (quintet-like line shape) superimposed on a broad single line with a peak to peak width (ΔHpp) of 22-25 G. The former decays much faster than the latter and their half-lives at room temperature are approximately 3.5 minutes and 600 minutes, respectively. As the decay temperature rises, the fraction of fast-decaying species increases. This phenomenon may be explained by the existence of crosslink density distribution. The increase in the concentration of long-lived radicals with increasing curing temperature, radiation dose and, to a less extent, curing time is also attributed to an increase in crosslink density of the epoxy network. The fast-decaying species are most likely associated with reactive radicals such as $CH_2-\overset{\bullet}{\underset{|}{C}}-CH_2-$,

$-\overset{\bullet}{C}H_2$ or $-\overset{H}{\underset{|}{\overset{|}{\underset{OH}{C}}}}\cdot$ trapped in regions of varying crosslink density. Some of the radicals react with oxygen probably producing alkoxy ($-\overset{|}{\underset{|}{C}}O\cdot$) or peroxy ($-\overset{|}{\underset{|}{C}}OO\cdot$) radicals.

An additional narrow ESR component ($\Delta Hpp=13G$), which is not observed for the epoxy sample irradiated at $77°K$, results when the sample is irradiated at

room temperature with doses more than 100 Mrad. This narrow component is ten-

tatively attributed to acyl type radicals ($-\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}\cdot$) which are probably produced at higher temperature in the presence of dissolved oxygen. However, peroxy type radicals are not ruled out as possible species responsible for the narrow ESR component.

A large concentration of electron spins (> 10^{20} spins/g) were found in the unirradiated T-300 graphite fiber and T300/5208 composites. Due to the symmetric line shape and no occurrence of power-saturation at around 2.0 mW microwave power, these unpaired electrons are assumed to be associated with free radicals in the graphite fiber. If this is true, interactions between these radicals and those generated in the irradiated epoxy may occur at the graphite fiber/epoxy interface and enhance the interfacial strength of the composite as a result of irradiation.

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LIST OF FIGURE TITLES

Figure 1. ESR spectra of TGDDM-DDS epoxy γ-irradiated with a dose of 100 Mrad (a) as-irradiated in liquid nitrogen (77°K), (b) after 200 min exposure of (a) to air at room temperature, (c) as-irradiated at room temperature in air, and (d) after 27 days exposure of (c) to air at room temperature. Samples were cured at 150°C (1 hr) and then at 177°C (5 hr). The spectra were measured at 77°K.

Figure 2. ESR spectra of TGDDM-DDS epoxy γ-irradiated with a dose of 800 Mrad at room temperature (23°C), (1) in vacuum-sealed ESR tube, (2) in air, and (3) spectrum-1 after exposure to air at room temperature for 90 days. Spectra were measured at room temperature.

Figure 3. ESR spectra of TGDDM-DDS epoxy irradiated with a 5 Mrad dose of γ-radiation in liquid nitrogen (77°K), (a) as-irradiated, (b) after 5 min exposure and (c) after 200 min exposure to air at room temperature.

Figure 4. The difference spectrum between spectrum-a and spectrum-b in Figure 3.

Figure 5. Isothermal decay of radicals in irradiated TGDDM-DDS epoxy in air at various temperatures.

Figure 6. ESR spectra of (1) graphite fiber (~1 mg) and (2) T300/5208 composites (~40 mg) irradiated with a 9,000 Mrad dose of 0.5 MeV electrons at room temperature in air, and (3) TGDDM-DDS (~170 mg) epoxy γ-irradiated with 5 Mrad and exposed to air for several months.

a   AS-IRRADIATED

(2.5 x 10^{19} spins/g)

b   AFTER 200 MIN

(0.5 x 10^{19} spins/g)

c   AS-IRRADIATED

(X 4)

(~0.5 x 10^{19} spins/g)

d   AFTER 27 DAYS

(X 10)

20 G
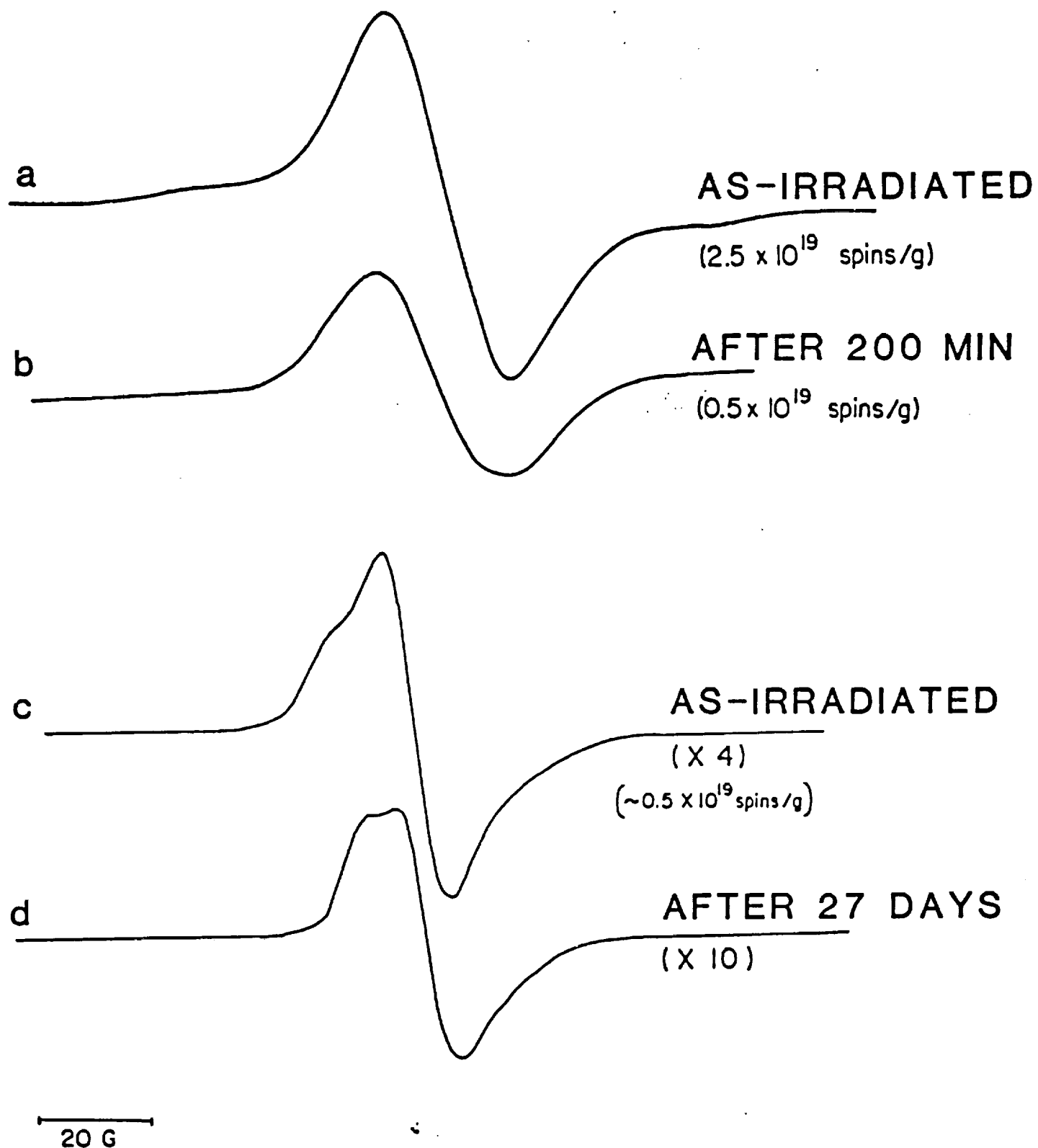
Fig 1
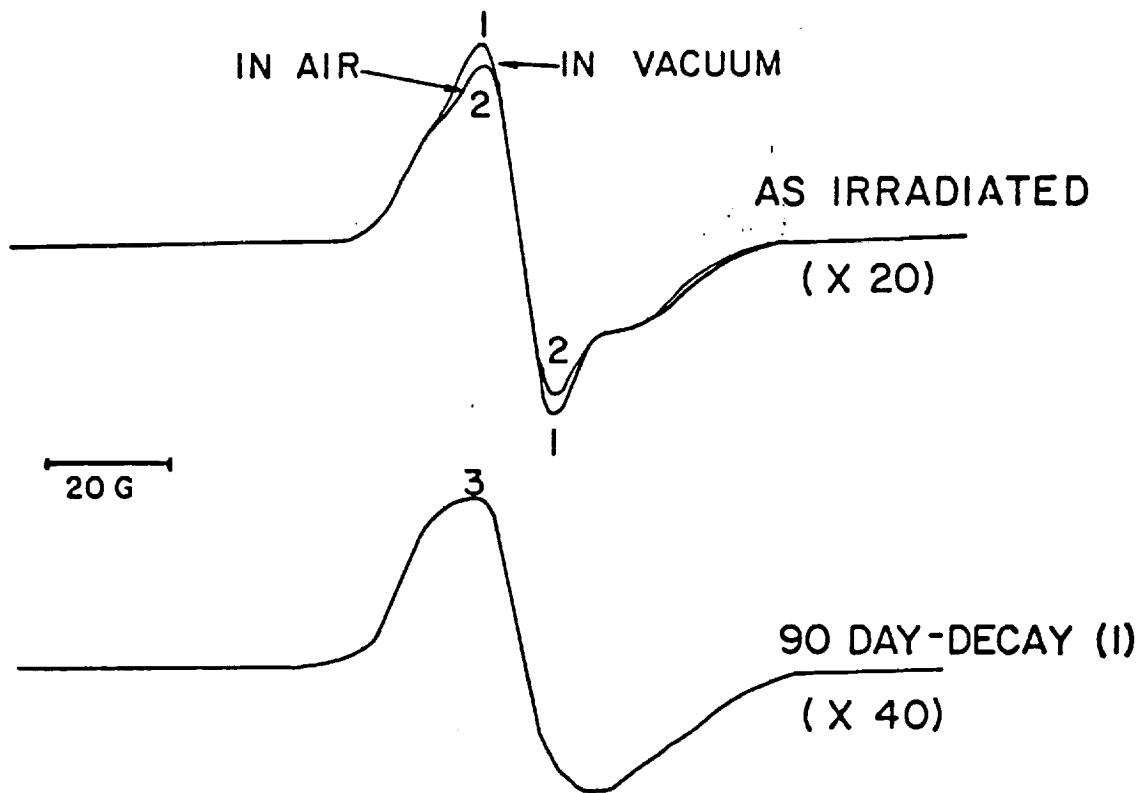
Figure 2 ESR spectra of TGDDM-DDS epoxy γ-irradiated
with a dose of 800 Mrad at room temperature (300°K), (1) in
air, (2) in vacuum-sealed tube, and (3) spectrum-1 after
exposure to air at 300°K for 90 days.

γ-irradiated at 77°K
5 Mrad

As — IRRADIATED

(3.8 X 10^{18} spins/g)

AFTER 5 MINS.

(1.56 X 10^{18} spins/g)

AFTER 190 MINS.

(1.04 X 10^{18} spins/g)

20 G
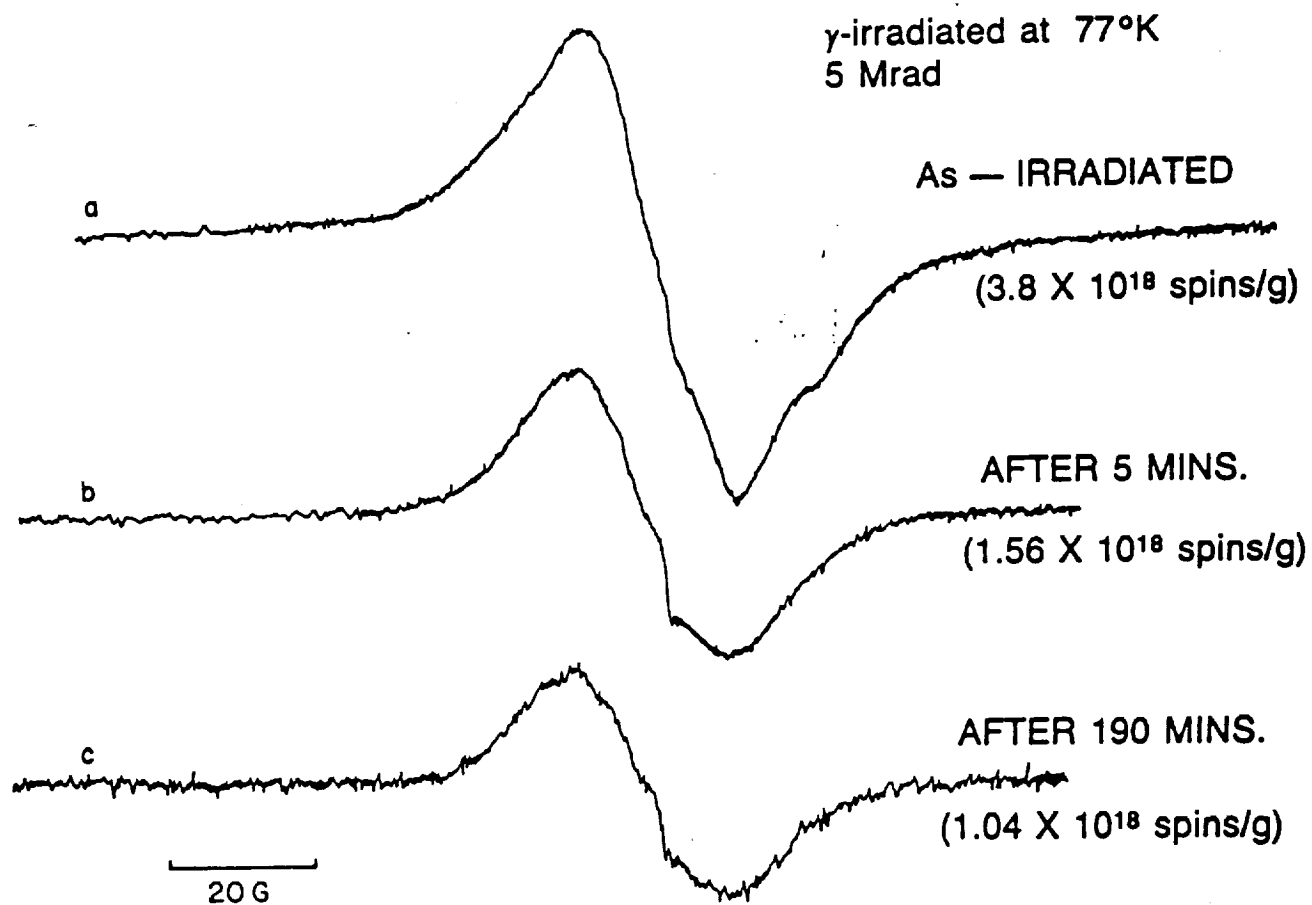
Figure   3   ESR spectra of TGDDM-DDS epoxy cured at 137°C (2 hrs) and then 160°C (5 hrs) and with a 5 Mrad dose of γ-radiation in liquid nitrogen (77°K). (a) as-irradiated (b) after 5 minute exposure to air at room temperature and (c) after 200 minute exposure.

23

DIFFERENCE SPECTRUM

20 G
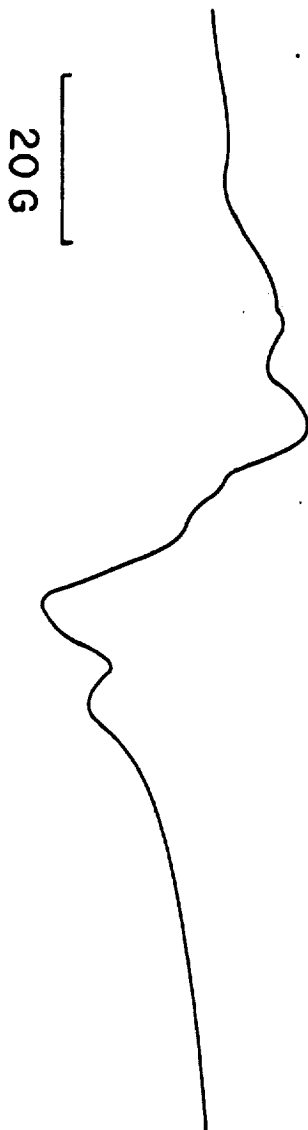
Figure 4   The difference spectrum between spectrum-a
and spectrum-b in Figure 4.8.
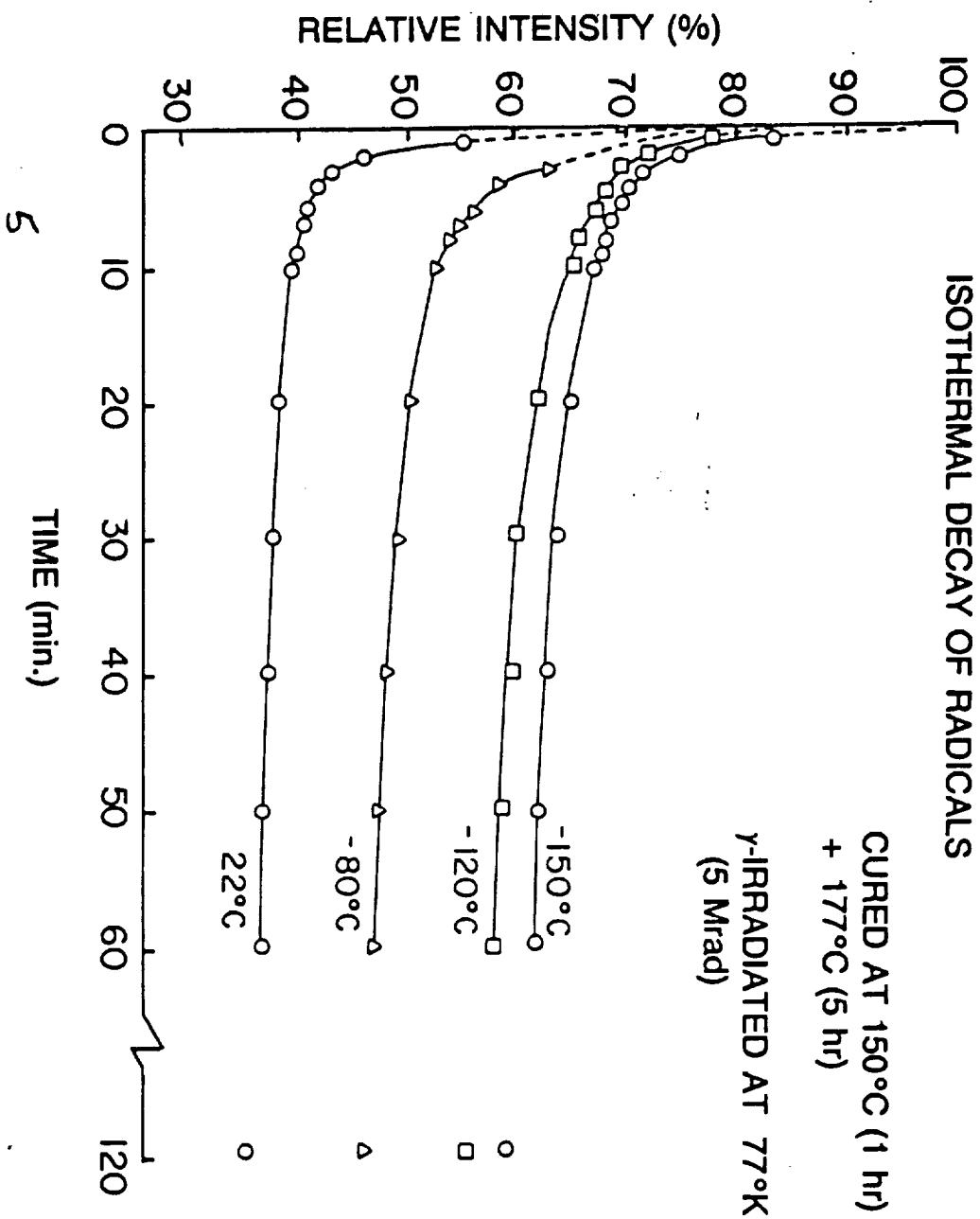
Figure 5   Isothermal decay of radicals in the irradiated
TGDDM-DDS epoxy.

1.- Graphite fiber
2- Composite
3- Epoxy
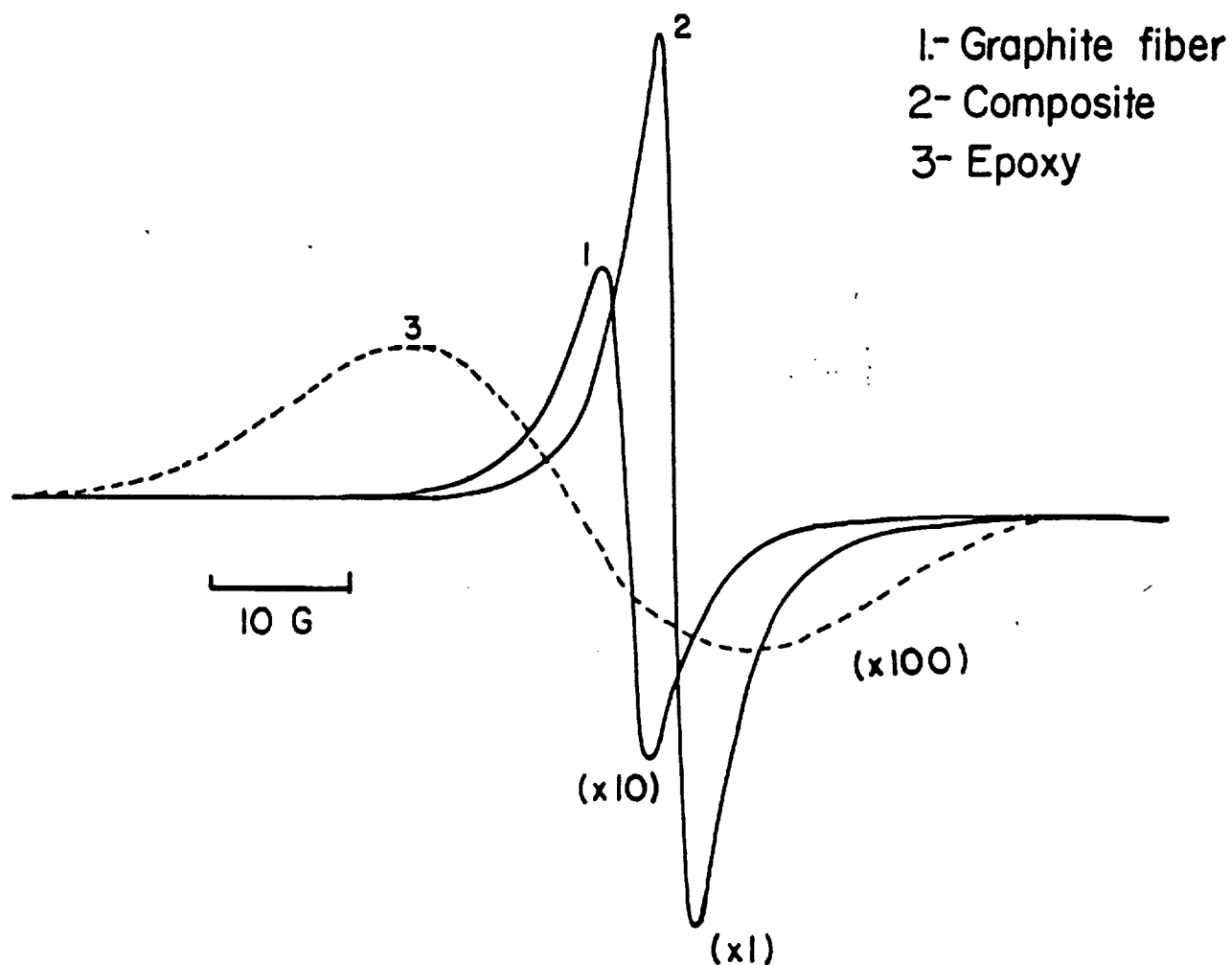
Fig 6 Figure. ESR spectra of (1) graphite fiber (~1 mg) and (2) T300/5208 composites (~4 mg) irradiated with a 9,000 Mrad dose of 1/2 MeV electrons at room temperature in air, and (3) TGDDM-DDS (~170 mg) epoxy γ-irradiated with 5 Mrad and exposed to air for several months.

Tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM)

4,4'-diaminodiphenyl sulfone (DDS)

$$\underset{\displaystyle OH}{\overset{\displaystyle H}{>N-CH_2-\underset{|}{\overset{|}{C}}-CH_2-N<}} \quad \longrightarrow \quad \underset{\displaystyle OH}{\overset{\displaystyle \bullet}{>N-CH_2-\underset{|}{\overset{|}{C}}-CH_2-N<}} + \bullet H \qquad (1)$$

$$\begin{array}{c} >N-CH_2-\overset{\bullet}{\underset{OH}{C}}-CH_2-N< \end{array} \xrightarrow{\text{O}_2} \begin{array}{c} \overset{\overset{\bullet}{O}}{\underset{|}{O}} \\ >N-CH_2-\overset{|}{\underset{OH}{C}}-CH_2-N< \end{array} \qquad (11)$$

$$(\text{III})$$

$$(\text{IV})$$

$$(\text{V})$$

$$>N-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-N< \quad \xrightarrow{\quad\rightsquigarrow\quad} \quad >N-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}\bullet \;+\; \bullet CH_2-N< \qquad (VI)$$

$$\overset{\diagup}{\underset{\diagdown}{N}}-CH_2-\overset{\overset{\textstyle\bullet}{\overset{\textstyle O}{\|}}}{\underset{\underset{\textstyle OH}{|}}{C}}-CH_2-\overset{\diagup}{\underset{\diagdown}{N}}\diagdown \quad \xrightarrow{\rotatebox{0}{$\sim\!\!\!\sim$}} \quad N-CH_2-\overset{\overset{\textstyle O}{\|}}{C}OH \ + \ \bullet CH_2-\overset{\diagup}{\underset{\diagdown}{N}}\diagdown \qquad (\text{VII})$$

$$\overset{>}{N}-CH_2-\overset{\bullet}{\underset{OH}{C}}-CH_2-N\overset{<}{} \xrightarrow{\quad\rightsquigarrow\quad} \overset{>}{N}-\overset{\bullet}{C}H_2 \; + \; \overset{H}{\underset{OH}{C}}{=}CH-N\overset{<}{} \qquad (VIII)$$